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ONE-DIMENSIONAL FLOW WITH CHEMICAL REACTION IN NOZZLE EXPANSIONS

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INTRODUCTION

The net jet thrust that is realizable from the flow of a reactive gas mixture through an expansion nozzle depends on the extent of recombination reactions, which yield chemical energy to be converted into kinetic energy of the exhaust stream. If no reaction occurs (frozen flow), the only enthalpy change involved is the summation of the sensible heat-content changes for each constituent of the mixture. If the mixture maintains equilibrium composition at each temperature and pressure throughout the expansion (equilibrium flow), enthalpy change results from heat of reaction as well as from sensible heat-content changes.

Frozen and equilibrium flow, then, represent two limits of the theoretical possible flows from a reactive mixture. It is important to know which of the flows to expect, or at what intermediate position between the two limits the actual flow will be. This is illustrated for a stoichiometric hydrocarbon-air mixture in figure 1.

This figure shows net jet thrusts for a hydrocarbon-burning ramjet at an altitude of 100,000 feet for a range of Mach numbers. The difference in net jet thrust between equilibrium and frozen expansion is marked especially at the higher Mach numbers.

Examination of the chemical constituents of such a hydrocarbon-air mixture at the elevated temperatures involved (up to 6500° R) shows that approximately 60 percent of the energy that is tied up in dissociated species can be linked to the CO molecule.

It is thus important to know, for the hydrocarbon-air system, whether CO will react fast enough to follow the equilibrium-flow path, or whether

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it will be so slow that frozen flow will be followed. Penner (ref. 1) has derived criteria for estimating whether flow will be "near equilibrium" or "near frozen". These criteria are useful as long as the reaction is either very fast or very slow so that either of his two limiting-flow criteria are satisfied. Unfortunately, however, the intermediate range where these limiting-flow criteria are not helpful is often large, so that recourse must be had to a more exact solution of the reaction-rate equation with the flow relations.

This report presents calculations for a system involving the constituents CO, O_2, CO_2, and an inert gas having the thermal properties of a mixture of N_2 and H_2O. The proportions of constituents are the same as those of a stoichiometric hydrocarbon-air system; however, only one overall reaction, that of $CO + \frac{1}{2} O_2 \rightleftharpoons CO_2$, is assumed to occur.

The results of calculations at simulated Mach numbers of 4, 7, and 10 are shown. The effect of uncertainties in the reaction rate constant are also shown.

A comparison of the results of the more exact calculations with interpretations based on Penner's criteria is presented.

Modes of energy storage other than chemical (for example, vibrational and rotational modes) were assumed to be at equilibrium.

Finally, the extent of entropy change in the nonequilibrium reacting gas flow is discussed.

BASIC EQUATIONS AND ASSUMPTIONS

One-dimensional, adiabatic, frictionless flow is assumed. The system consists of the constituents CO, CO_2, O_2, H_2O, and N_2 in the proportions that would exist in stoichiometric hydrocarbon-air mixture. The only reaction considered is the over-all reaction

$$CO + \frac{1}{2} O_2 \rightleftharpoons CO_2 \tag{1}$$

The following system of equations set up for simultaneous solution are given. (Symbols are defined in appendix A.)

Ideal gas relation,

$$\frac{dp}{p} - \frac{d\rho}{\rho} - \frac{dT}{T} + \frac{d\overline{m}}{\overline{m}} = 0 \tag{2}$$

Continuity,

$$\frac{d\rho}{\rho} + \frac{dA}{A} + \frac{du}{u} = 0 \tag{3}$$

Momentum,

$$dp + \frac{\rho}{2g_c} du^2 = 0 \tag{4}$$

Energy,

$$d \sum_{i=1}^{n} \frac{y_i}{m_i} H_i(T) + \frac{1}{2g_c J} du^2 = 0 \tag{5}$$

Molecular weight,

$$\frac{1}{\overline{m}} = \sum \frac{y_i}{m_i} \tag{6}$$

Stoichiometric relations,

$$d\left(\frac{y_{CO}}{m_{CO}}\right) = 2d\left(\frac{y_{O_2}}{m_{O_2}}\right) = -d\left(\frac{y_{CO_2}}{m_{CO_2}}\right) \tag{7}$$

Velocity-time relation (one-dimensional flow assumption),

$$dx = u\, d\theta \tag{8}$$

Nozzle shape,

$$A = \pi r^2 = f(x) \tag{9}$$

where

$$r = 0.4167 - 0.5743x \quad \text{for} \quad 0 < x \leq 0.29$$

$$r = 0.75 - \left[1.18x - x^2 - 0.0088\right]^{1/2} \quad \text{for} \quad 0.29 \leq x \leq 0.67$$

$$r = 0.0792 + 0.1386x \quad \text{for} \quad 0.67 \leq x \leq 1.25$$

(This is simply a conical-shaped inlet and exit with a circular throat section.)

Reaction rate,

$$\frac{1}{m_{CO}} \frac{dy_{CO}}{d\theta} = \frac{k_f}{\rho} \left[\left(\frac{\rho y_{CO}}{m_{CO}}\right)\left(\frac{\rho y_{O_2}}{m_{O_2}}\right) - \frac{1}{K}\left(\frac{\rho y_{CO_2}}{m_{CO_2}}\right)\left(\frac{\rho y_{O_2}}{m_{O_2}}\right)^{1/2} \right] \tag{10}$$

Equation (10) was written to express the net rate of reaction (1) so that the system could approach the equilibrium-flow conditions. The possible errors of relating the forward and reverse rates to the equilibrium constant for an over-all reaction in this way are discussed in reference 2.

The value used for the rate constant was taken from reference 3 and is expressed

$$\left[k_f\right]_{ref} = 1.2\times10^9 \, e^{-\frac{24000}{RT}}, \quad \frac{\text{liter}}{(\text{gm mol})(\text{sec})} \tag{11}$$

The rate was assumed inversely proportional to density, as pointed out in reference 3. An average value of the density was taken from the tabulated data and the rate-constant expression used was

$$k_f = 7.9\times10^6 \, \frac{\overline{m}}{\rho} \, e^{\frac{-21,740}{T}} \, \frac{\text{cu ft}}{(\text{lb mol})(\text{sec})} \tag{12}$$

Enthalpy and equilibrium constant data from reference 4 were used.

The method used for the solution of the differential equations was as follows: For small intervals of time, the change in composition is computed from the kinetic rate expression based on the previous (or initial) calculation, using Worthy's method (ref. 5). Knowing the composition across the interval, the total enthalpy is computed for an assumed temperature drop. The change in velocity is then computed from the energy equation. Pressure, density, and area are computed using the momentum, state, and continuity equations, respectively. This computed area is tested against the nozzle area at this point. If they do not agree to the desired accuracy, a new temperature for the interval is assumed, and the computations are repeated until the desired agreement is attained. At the throat, it may be impossible to compute an area that will fit the actual nozzle area, for the specified initial conditions; then a new initial velocity is assumed and the problem is recomputed from the inlet of the nozzle.

The system of only five constituents with but one over-all reaction assumed is, of course, a crude simulation of the actual hydrocarbon-air combustion system. Since the carbon monoxide oxidation, however, is certain to be of major importance in the expansion of hydrocarbon combustion products, it was hoped that the simulated system would give some engineering estimates of the over-all performance of the real gas mixture.

It may be noted that since the CO oxidation reaction represents only approximately 60 percent of the energy tied up in dissociated species in the

hydrocarbon-air system, the real-gas equilibrium flow will yield somewhat different temperatures and compositions than the equilibrium flow for the system assumed. The frozen-flow results are nearly identical for either case.

The conditions, which were assumed for the nozzle inlet, were temperatures and pressures (table I) corresponding to the indicated flight Mach numbers at 100,000 feet and a diffuser kinetic-energy efficiency of 0.875. The CO-O_2-CO_2 compositions were assumed to be in equilibrium at the nozzle inlet.

RESULTS OF CALCULATIONS

The results of the calculations for the 15-inch long nozzle at inlet conditions corresponding to flight Mach numbers of 4, 7, and 10 are shown in figures 2(a) to (c). The variation of the weight fraction of CO with axial distance along the nozzle with reaction occurring according to equations (10) and (11) is compared with complete frozen and equilibrium expansions. At a Mach 4 flight condition, the composition is close to frozen throughout the expansion. As the flight Mach number increases, with attendant increases in temperature and pressure, the composition tends more and more toward the equilibrium values. At Mach 10, however, the flow is still only about midway between the frozen and equilibrium values (fig. 2(c)).

It was of interest to know what effect a variation in the reaction rate constant k_f would have on the flow. This would indicate the accuracy required in knowledge of reaction rates, which would substantially

affect the flow. The effects of five- and ten-fold increases in the value of k_f on the flow at the Mach 4 condition and of a five-fold increase at the Mach 7 conditions are shown in figures 3(a) and (b), respectively. These increases affect the extent of reaction considerably, but near-equilibrium flow is not reached at any of these conditions.

The curves of figures 2 and 3 are for a nozzle that is 15 inches long. Presumably a ten-fold increase in the nozzle length would be equivalent to a ten-fold increase in reaction rate. Calculations were carried out for a nozzle which was ten times longer than the previous calculation. These results are shown in figure 4. It can be seen that the same performance curve results with either the short nozzle with the reaction rate increased by a factor of ten, or with the longer nozzle at the normal reaction rate.

The static-temperature variations through the nozzle accompanying these concentration changes are shown in figures 5(a) to (c).

The calculations were performed on an electronic digital computer. Accuracy of the numerical integration was estimated by varying the step size and integration method, and the integration was well within that required for engineering purposes.

Comparison of Results With Penner's Criteria

It was also considered of interest to compare the calculations with the predictions of "near-equilibrium" and "near-frozen" flow by the criteria derived by Penner (ref. 1).

In reference 1 the following relations are derived:

(1) Near-equilibrium flow criterion.

Flow is near equilibrium if

$$T' - T = -\left(\frac{DT}{D\theta}\right) z \leq 36^{\circ}\ R \tag{13}$$

where $-(DT/D\theta)$ is the rate of change of temperature with time in the nozzle and z is a reaction time.

$$z = \left\{ k_f' \rho^{n'-1} \left[\prod_{j=1}^{n} \left(\frac{y_j}{m_j}\right)^{v_j'}\right]\left[\sum_{i=1}^{n} (v_i'' - v_i')^2 \frac{m_i}{y_i}\right] \right\}^{-1} \tag{14}$$

For the reaction

$$CO + \frac{1}{2} O_2 \rightleftharpoons CO_2$$

$$z = \left\{ k_f' \left(\frac{P}{JRT}\right)^{1/2} \left(\frac{y_{CO}}{28}\right)\left(\frac{y_{O_2}}{32}\right)^{1/2} \left[\frac{44}{y_{CO_2}} + \frac{28}{y_{CO}} + \frac{32}{4y_{O_2}}\right]\right\}^{-1} \tag{14a}$$

(2) Near-frozen criterion.

Flow is near frozen if

$$\frac{T_c - T'}{T_c - T} \cong \frac{1}{(T' - T)\left(\frac{d \ln K_y}{dT}\right)_{T_c}} \leq 0.01 \tag{15}$$

Values of $(T' - T)$ and $(T_c - T')/(T_c - T)$ were calculated at several points in the nozzle and these values are plotted in figure 6. These values were calculated using only the temperature profile of the limiting flows and the initial equilibrium conditions, since these data would be known without the rigorous calculation procedure.

From examination of the curves of figures 6(a) and (b) and assuming the previously mentioned criterion values, the following conclusions might be drawn:

(1) At Mach 4, flow at no time is near-equilibrium. Beyond $x = 0.4$ the flow is near frozen.

(2) At Mach 7, flow is near-equilibrium to $x = 0.2$ feet and near-frozen beyond $x = 0.8$ feet.

(3) At Mach 10, flow is near-equilibrium to about 0.4 feet. Flow does not approach near-frozen anywhere in the nozzle.

A comparison of these conclusions with the calculated concentrations shown in figures 2(a) to 2(c) indicates that the near-limiting flow criteria of Penner gives a reasonable picture of the flow behavior. It is clear, however, that they alone are not sufficient to define the flow in the large regime in between which neither limiting flow criterion is satisfied.

Entropy

Discussions have appeared in the literature from time to time regarding the entropy change that occurs in the expansion of a reacting gas mixture through a nozzle. Occasionally the assumption of constant entropy has been made for the non-equilibrium reaction case.

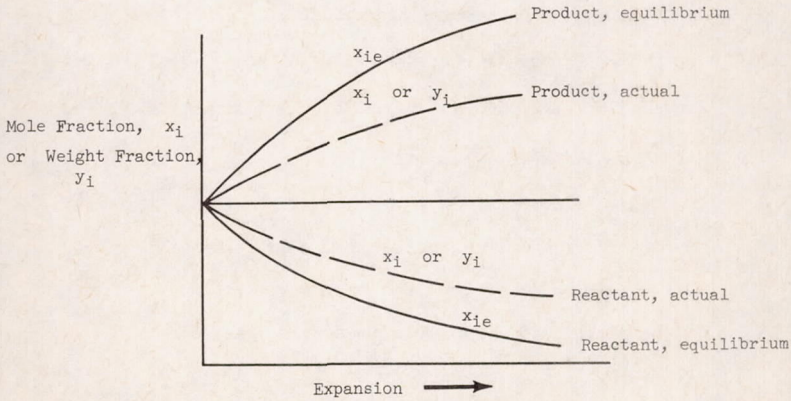
The following relation, derived in the appendix, shows that for the reacting case, not at equilibrium, an entropy increase occurs.

$$\frac{dS}{R} = \sum_{i=1}^{n} (\ln x_{ie} - \ln x_i) \frac{dy_i}{m_i} \tag{16}$$

If the mixture follows equilibrium flow, $x_i = x_{ie}$ and the entropy change is zero.

If the composition remains fixed (frozen), all values of dy_i are zero and the flow is also isentropic.

For cases where reaction occurs, but the rate is too slow to follow equilibrium, an entropy increase occurs. This can be seen in the following illustration:



For the products, both $(\ln x_{ie} - \ln x_i)$ and dy_i are positive.

For the reactants, both $(\ln x_{ie} - \ln x_i)$ and dy_i are negative.

Hence, for the non-equilibrium reaction,

$$\frac{dS}{R} > 0 \tag{17}$$

The relation of equation (16) can be shown to be equivalent to one derived in reference 6.

APPENDIX A

SYMBOLS

A	area, sq ft
A,B,C,D	chemical species
a,b,c,d	stoichiometric coefficients
Cp_i	molar specific heat of component i, $\frac{\text{Btu}}{(\text{lb mole})(^{\circ}\text{R})}$
$f(x)$	function describing nozzle shape
g_c	conversion constant, $32.19 \frac{\text{lb(mass)/ft}}{\text{lb(force)/sec}^2}$
$H_i(T)$	enthalpy per mole of constituent i at temperature T, $\frac{\text{Btu}}{\text{lb mole}}$
ΔH_r	heat of reaction per a moles of constituent A, $\frac{\text{Btu}}{\text{lb mole}}$
J	conversion factor, $\frac{\text{ft lb(F)}}{\text{Btu}}$
K	equilibrium constant
K_p	equilibrium constant based on pressures, $(\text{atm})^{\Delta n}$
K_x	equilibrium constant based on mole fractions
K_y	equilibrium constant based on weight fractions
k_f	forward reaction rate constant, $\left(\frac{\text{cu ft}}{\text{lb mole}}\right) \text{sec}^{-1}$
k_f'	(in eq. (14)), $k_f' = \frac{d \ln[CO]}{d\theta} [O_2]^{1/2}$, $\left(\frac{\text{cu ft}}{\text{lb mole}}\right)^{1/2} \text{sec}^{-1}$, where $[\ ]_i = \frac{y_i \rho}{m_i}$
M_0	flight Mach number
m_i or m_j	molecular weight of component i or j, $\frac{\text{lb(M)}}{\text{lb mole}}$
$\bar{m}$	mean molecular weight, $\frac{\text{lb(M)}}{\text{lb mole}}$
n_i	number of moles of i

n'	order of forward reaction
P	pressure, atm
p	pressure, $\frac{\text{lb}}{\text{sq ft}}$
Q_A	heat of reaction per unit weight of constituent A, $\frac{\text{Btu}}{\text{lb(M)}}$
R	universal molar gas constant, $\frac{\text{Btu}}{(\text{lb mole})(^{\circ}\text{R})}$
r	radius, ft
$S_i^{\circ}(T)$	molar entropy of constituent i at 1 atm and temperature T, $\frac{\text{Btu}}{(\text{lb mole})(^{\circ}\text{R})}$
$S(T,p)$	molar entropy of mixture at (T,p), $\frac{\text{Btu}}{(\text{lb mole})(^{\circ}\text{R})}$
ΔS_r°	entropy change for reaction with reactants and products at one atm., $\frac{\text{Btu}}{(\text{lb mole})(^{\circ}\text{R})}$
T	static temperature of system, $^{\circ}$R
T'	fictitious temperature relating to near-equilibrium flow, $^{\circ}$R
T_c	nozzle inlet temperature, $^{\circ}$R
u	velocity, ft/sec
v_i', v_i''	stoichiometric coefficients
x	linear distance, ft
x_i	mole fraction of constituent i
x_{ie}	mole fraction of constituent i at equilibrium at existing (T,p)
y_i	mass fraction of constituent i
z	reaction time, sec
θ	time, sec
ρ	mass density of mixture, $\frac{\text{lb(M)}}{\text{cu ft}}$

APPENDIX B

DERIVATION OF EXPRESSION FOR ENTROPY CHANGE IN NOZZLE FLOW WITH CHEMICAL REACTION

Adiabatic, frictionless flow of an ideal gas mixture is assumed. The flow is not required to be in chemical equilibrium, nor chemically frozen. The following general reaction is assumed

$$aA + bB \rightleftharpoons cC + dD \tag{B1}$$

The momentum equation is

$$\frac{dp}{\rho} + \frac{du^2}{2g_c} = 0 \tag{B2}$$

The energy equation for constant energy per unit mass is

$$\sum y_i \frac{Cp_i}{m_i} dT + Q_A dy_A + \frac{du^2}{J2g_c} = 0 \tag{B3}$$

where Q_A is the heat of reaction (eq. (B1)) per unit mass of A. Combining equations (B2) and (B3) gives

$$\rho \sum y_i \frac{Cp_i}{m_i} dT + \rho Q_A dy_A - \frac{1}{J} dp = 0 \tag{B4}$$

The ideal gas law is

$$\frac{\rho}{p} = \frac{\bar{m}}{JRT} \tag{B5}$$

Substitution of equation (B5) into (B4) yields

$$\frac{\bar{m}}{RT} \sum y_i \frac{Cp_i}{m_i} dT + \frac{\bar{m}}{RT} Q_A dy_A - \frac{dp}{p} = 0 \tag{B6}$$

Mole fractions and weight fractions for a mixture are related through

$$y_i = x_i \frac{m_i}{\bar{m}} \tag{B7}$$

Hence, equation (B6) can be expressed as

$$\sum x_i \frac{Cp_i}{RT} dT + \frac{\bar{m}}{RT} Q_A \, dy_A - \frac{dp}{p} = 0 \qquad (B8)$$

The entropy of a mixture of ideal gases at any temperature and pressure is

$$S(T,p) = \sum x_i S_i^o(T) - R \ln P - R \sum x_i \ln x_i \qquad (B9)$$

where S is molar entropy

Differentiating and dividing by R yields

$$\frac{dS}{R} = \sum x_i \frac{dS_i^o}{R} + \sum \frac{S_i^o}{R} dx_i - \frac{dp}{p} - \sum \ln x_i \, dx_i \qquad (B10)$$

But,

$$dS_i^o = Cp_i \frac{dT}{T} \qquad (B11)$$

Thus, equation (B10) is

$$\frac{dS}{R} = \sum \frac{x_i CP_i \, dT}{RT} + \sum \frac{S_i^o}{R} dx_i - \frac{dp}{p} - \sum \ln x_i \, dx_i \qquad (B12)$$

Substitution of equation (B8) into (B12) yields the following equation for entropy change occurring during expansion

$$\frac{dS}{R} = - \frac{\bar{m}}{RT} Q_A \, dy_A + \sum \frac{S_i^o}{R} dx_i - \sum \ln x \quad dx_i \qquad (B13)$$

For reaction (B1),

$$Q_A = \frac{\Delta H_r}{am_A} \qquad (B14)$$

where ΔH_r is the heat of reaction for a moles of A

Thus,

$$\frac{\bar{m}}{RT} Q_A \, dy_A = \frac{\bar{m}}{am_A} \frac{\Delta H_r}{RT} dy_A \qquad (B15)$$

For reaction (B1), also, the equilibrium constant may be written as

$$K_x = \frac{x_{Ce}^c x_{De}^d}{x_{Ae}^a x_{Be}^b} \tag{B16}$$

Since there may be a change in the number of moles during reaction,

$$K_p = K_x P^{\Delta n} \tag{B17}$$

where

$$\Delta n = (c + d) - (a + b) \tag{B18}$$

Thus,

$$\ln K_p = c \ln x_{Ce} + d \ln x_{De} - a \ln x_{Ae} - b \ln x_{Be} + \Delta n \ln P \tag{B19}$$

But,

$$\ln K_p = \frac{\Delta H_r}{RT} + \frac{\Delta S_r^o}{R} \tag{B20}$$

where ΔS_r^o is the entropy change for the reaction with reactants and products at standard pressure.

Substituting equations (B20) and (B14) into (B13) yields

$$\frac{dS}{R} = -\frac{\bar{m}}{am_A}\left(\ln K_p - \frac{\Delta S_r^o}{R}\right) dy_A + \sum \frac{S_i^o}{R} dx_i - \sum \ln x_i \, dx_i \tag{B21}$$

Conditions of stoichiometry and equation (B7) can be combined to yield the equality,

$$dy_A = \frac{m_A}{\bar{m}}\left(dx_A - x_A \frac{d\bar{m}}{\bar{m}}\right) = \frac{m_A}{\bar{m}} \frac{a}{b}\left(dx_B - x_B \frac{d\bar{m}}{\bar{m}}\right)$$

$$= -\frac{m_A}{\bar{m}} \frac{a}{c}\left(dx_C - x_C \frac{d\bar{m}}{\bar{m}}\right) = -\frac{m_A}{\bar{m}} \frac{a}{d}\left(dx_D - x_D \frac{d\bar{m}}{\bar{m}}\right) \tag{B22}$$

The first term of the right side of equation (B21) can be converted, through relations (B19) and (B22), to

$$- \frac{\bar{m}}{am_A}\left(\ln K_p - \frac{\Delta S_r^o}{R}\right) dy_A = - \frac{\bar{m}}{am_A}\Bigg\{(c \ln x_{Ce})\left(- \frac{m_A}{\bar{m}}\frac{a}{c}\right)\left(dx_C - x_C \frac{d\bar{m}}{\bar{m}}\right) +$$

$$(d \ln x_{De})\left(- \frac{m_A}{\bar{m}}\right)\left(\frac{a}{d}\right)\left(dx_D - x_D \frac{d\bar{m}}{\bar{m}}\right) - (a \ln x_{Ae})\left(\frac{m_A}{\bar{m}}\right)\left(dx_A - x_A \frac{d\bar{m}}{\bar{m}}\right) -$$

$$(b \ln x_{Be})\left(\frac{m_A}{\bar{m}}\frac{a}{b}\right)\left(dx_B - x_B \frac{d\bar{m}}{\bar{m}}\right) + \Delta n \ln P \, dy_A -$$

$$\left(c \frac{S_C^o}{R}\right)\left(- \frac{m_A}{\bar{m}}\frac{a}{c}\right)\left(dx_C - x_C \frac{d\bar{m}}{\bar{m}}\right) - \left(\frac{dS_D^o}{R}\right)\left(- \frac{m_A}{\bar{m}}\frac{a}{d}\right)\left(dx_D - x_D \frac{d\bar{m}}{\bar{m}}\right) +$$

$$a\left(\frac{S_A^o}{R}\right)\left(\frac{m_A}{\bar{m}}\right)\left(dx_A - x_A \frac{d\bar{m}}{\bar{m}}\right) + \left(\frac{bS_B^o}{R}\right)\left(\frac{m_A}{\bar{m}}\frac{a}{b}\right)\left(dx_B - x_B \frac{d\bar{m}}{\bar{m}}\right)\Bigg\} \quad \text{(B23)}$$

Or in simplified form,

$$- \frac{\bar{m}}{am_A}\left(\ln K_p - \frac{\Delta S_r^o}{R}\right) dy_A = \sum \ln x_{ie} \, dx_i - \sum x_i \ln x_{ie} \frac{d\bar{m}}{\bar{m}} +$$

$$\sum \frac{x_i S_i^o}{R} \frac{d\bar{m}}{\bar{m}} - \sum \frac{S_i^o}{R} dx_i - \frac{\bar{m}}{am_A} \Delta n \ln P \, dy_A \quad \text{(B24)}$$

Substitution of equation (B24) into (B21) yields

$$\frac{dS}{R} = \sum \ln x_{ie} \, dx_i - \sum \ln x_i \, dx_i - \sum x_i \ln x_{ie} \frac{d\bar{m}}{\bar{m}} +$$

$$\sum x_i \frac{S_i^o}{R} \frac{d\bar{m}}{\bar{m}} - \frac{\bar{m}}{am_A} \Delta n \ln P \, dy_A \quad \text{(B25)}$$

The last term of equation (B25) may be reduced as follows:

$$- \frac{\bar{m}}{am_A} \Delta n \ln P \, dy_A = - \frac{\bar{m}}{am_A} \Delta n \ln P \left(\frac{m_A}{\bar{m}}\right)\left(dx_A - x_A \frac{d\bar{m}}{\bar{m}}\right) \quad \text{(B26)}$$

$$= -\left(\frac{c}{a} + \frac{d}{a} - \frac{a}{a} - \frac{b}{a}\right) \ln P \left(dx_A - x_A \frac{d\bar{m}}{\bar{m}}\right) \tag{B27}$$

Again substituting the identities from stoichiometric relations yields

$$- \frac{\bar{m}}{a\bar{m}} \Delta n \ln P \, dy_A = \ln P \left[dx_C - x_C \frac{d\bar{m}}{\bar{m}} + dx_D - x_D \frac{d\bar{m}}{\bar{m}} + dx_A - x_A \frac{d\bar{m}}{\bar{m}} + dx_B - x_B \frac{d\bar{m}}{\bar{m}}\right] \tag{B28}$$

$$= \ln P \left[\sum dx_i - \sum x_i \frac{d\bar{m}}{\bar{m}}\right] \tag{B29}$$

$$= - \ln P \frac{d\bar{m}}{\bar{m}} \tag{B30}$$

Substitution of relation (B30) into (B25) yields

$$\frac{dS}{R} = \sum (\ln x_{ie} - \ln x_i) \, dx_i + \left[\sum x_i \frac{S_i^o}{R} - \ln P\right] \frac{d\bar{m}}{\bar{m}} - \sum x_i \ln x_{ie} \frac{d\bar{m}}{\bar{m}} \tag{B31}$$

If the term $\sum x_i \ln x_i \frac{d\bar{m}}{\bar{m}}$ is added to and subtracted from equation (B30) the terms are rearranged,

$$\frac{dS}{R} = \left[\sum x_i \frac{S_i^o}{R} - \ln P - \sum x_i \ln x_i\right] \frac{d\bar{m}}{\bar{m}} + \sum (\ln x_{ie} - \ln x_i) \, dx_i - \sum (x_i \ln x_{ie} - x_i \ln x_i) \frac{d\bar{m}}{\bar{m}} \tag{B32}$$

or

$$\frac{dS}{R} = \frac{S}{R} \frac{d\bar{m}}{\bar{m}} + \sum (\ln x_{ie} - \ln x_i) \, dx_i - \sum (x_i \ln x_{ie} - x_i \ln x_i) \frac{d\bar{m}}{\bar{m}} \tag{B33}$$

Entropy per mole has been used. The entropy per unit mass is $(S/\overline{m})$. Hence,

$$\frac{d(S/\overline{m})}{R} = \frac{1}{\overline{m}}\left[\frac{dS}{R} - \frac{S}{R}\frac{d\overline{m}}{\overline{m}}\right] \tag{B34}$$

Equation (B33) can then be expressed as

$$\frac{d(S/\overline{m})}{R/\overline{m}} = \sum(\ln x_{ie} - \ln x_i)\, dx_i - \sum(x_i \ln x_{ie} - x_i \ln x_i)\frac{d\overline{m}}{\overline{m}} \tag{B35}$$

From equation (B7), differentiating yields

$$dy_i = \frac{m_i}{\overline{m}}\left(dx_i - x_i\frac{d\overline{m}}{\overline{m}}\right) \tag{B36}$$

Rearranging equation (B35) gives

$$\frac{d(S/\overline{m})}{R/\overline{m}} = \sum \ln x_{ie}\left(dx_i - x_i\frac{d\overline{m}}{\overline{m}}\right) - \sum \ln x_i\left(dx_i - x_i\frac{d\overline{m}}{\overline{m}}\right) \tag{B37}$$

Substituting equation (B36) into (B37) yields

$$\frac{d(S/\overline{m})}{R/\overline{m}} = \overline{m}\left\{\sum \ln x_{ie}\frac{dy_i}{m_i} - \sum \ln x_i\frac{dy_i}{m_i}\right\} \tag{B38}$$

or

$$\frac{d(S/\overline{m})}{R/\overline{m}} = \overline{m}\sum(\ln x_{ie} - \ln x_i)\frac{dy_i}{m_i} \tag{B39}$$

Equation (B39) expresses the change in entropy for a reacting gas mixture during expansion.

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TABLE I. - CONDITIONS AT NOZZLE INLET

Simulated flight Mach number	Temperature, ^{o}R	Pressure, atm	Weight fraction		
			CO	O_2	CO_2
4	4575	0.52	0.0414	0.0202	0.1322
7	5430	3.4	.0685	.0287	.0863
10	6480	11.0	.0936	.0325	.0388

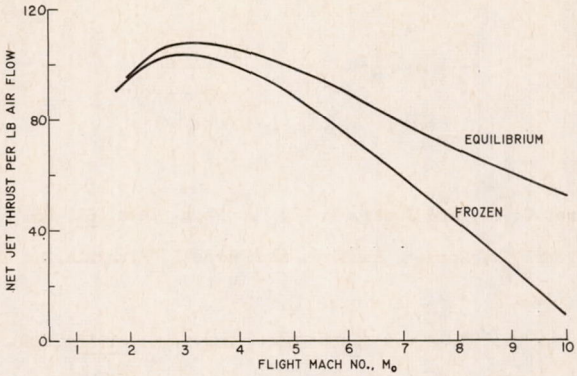
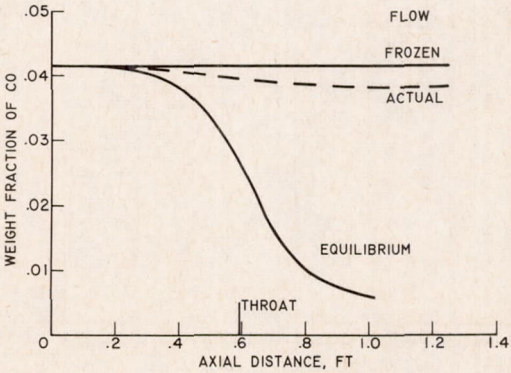
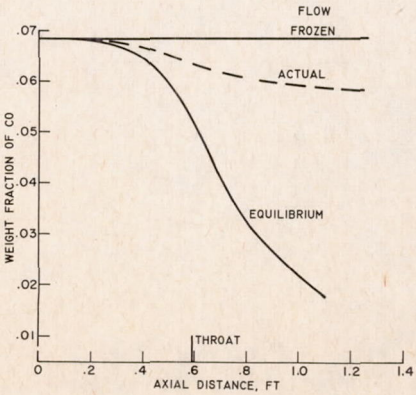


Fig. 1. - Variation of net jet thrust with equilibrium and frozen flow for several Mach numbers. Hydrocarbon, $(CH_2)_n$ + air; stoichiometric conditions; altitude, 100,000 feet; diffuser kinetic energy efficiency, 0.875.



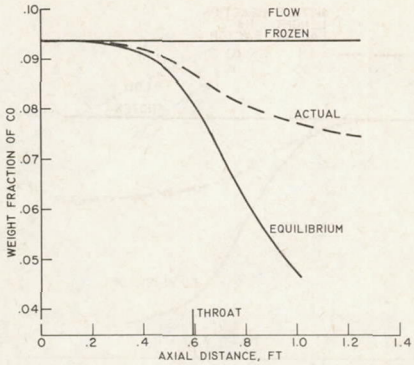
(a) Flight Mach number, 4.

Fig. 2. - Variation of CO concentration through nozzle.



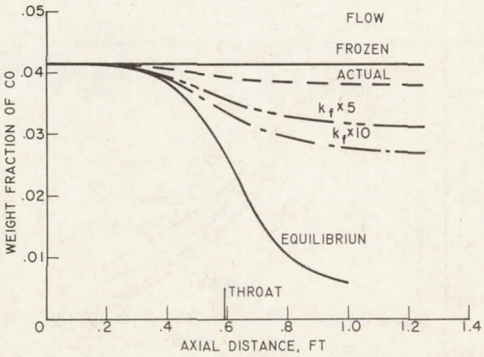
(b) Flight Mach number, 7.

Fig. 2. - Continued. Variation of CO concentration through nozzle.



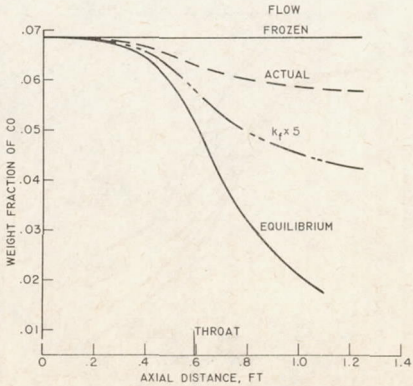
(c) Flight Mach number, 10.

Fig. 2. - Concluded. Variation of CO concentration through nozzle.



(a) Flight Mach number, 4.

Fig. 3. - Effect of reaction-rate change on variation of CO concentration through nozzle.



(b) Flight Mach number, 7.

Fig. 3. - Concluded. Effect of reaction-rate change on variation of CO concentration through nozzle.

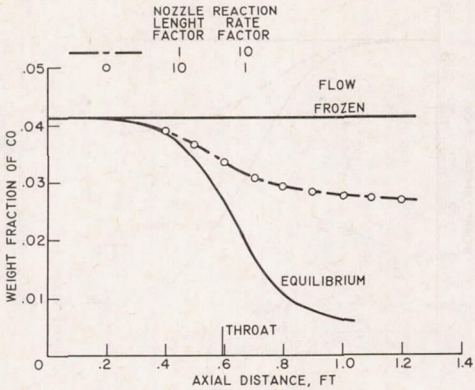
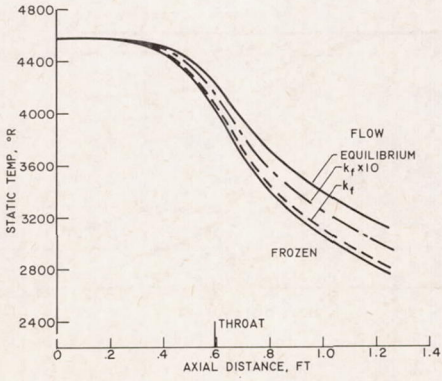
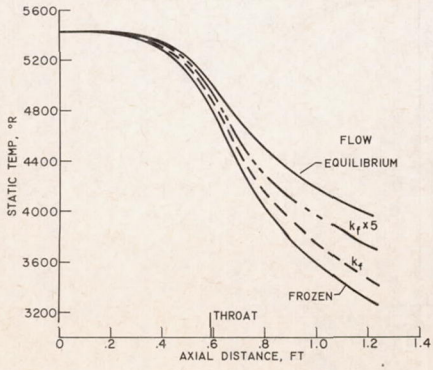


Fig. 4. - Comparison of reaction rate - residence time interchange on extent of reaction. Flight Mach number, 4.



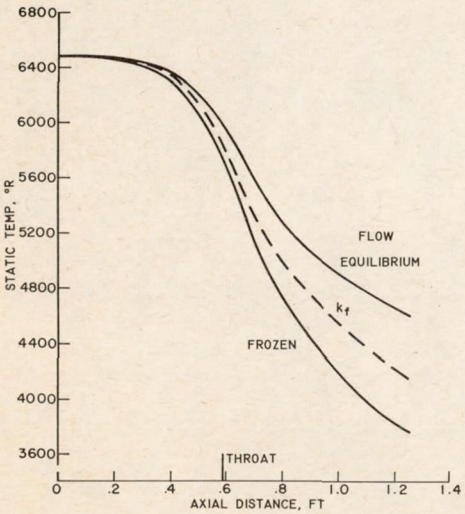
(a) Flight Mach number, 4.

Fig. 5. - Static-temperature variation through nozzle.



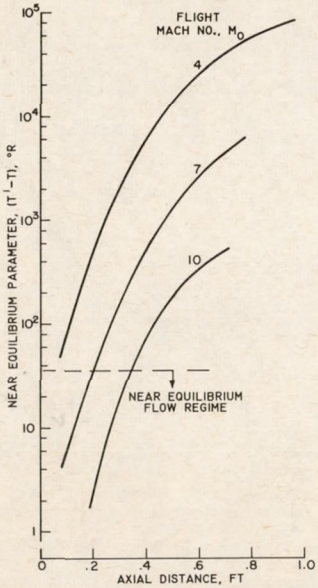
(b) Flight Mach number, 7.

Fig. 5. - Continued. Static-temperature variation through nozzle.



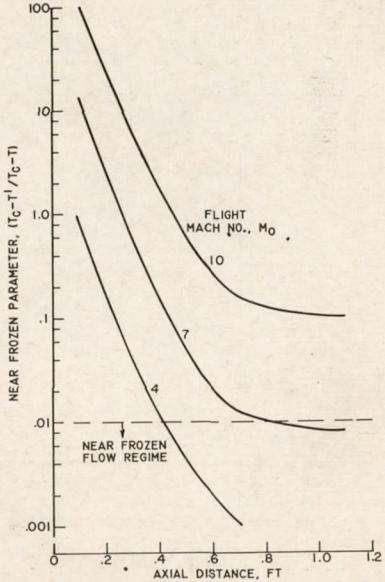
(c) Flight Mach number, 10.

Fig. 5. - Concluded. Static-temperature variation through nozzle.



(a) Near-equilibrium flow criteria.

Fig. 6. - Variation of near-limiting flow criteria through nozzle.



(b) Near-frozen flow criteria.

Fig. 6. - Concluded. Variation of near-limiting flow criteria through nozzle.

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